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ABSTRACT

A semiclassical reactive flux algorithm for calculating thermally activated rate constants is presented which is based on a semiclassical transition state theory due to Chapman, Garrett, and Miller [J. Chem. Phys. 63 (1975) 2710]. This reactive flux technique, when combined with the semiclassical TST, enables one to describe dynamical recrossings of the transition state on the same footing as tunneling effects. Most importantly, the method is readily applied to nonlinear multidimensional systems over a wide range of temperatures. It will be shown that the method works very well for a variety of existing models.

1. Introduction

It is highly desirable to have computational methods which allow for the efficient and accurate numerical evaluation of activated rate constants in complex systems. It is perhaps no surprise, therefore, that the preeminent theory of this sort—classical transition state theory (TST)—is one of the central theoretical tools in modern chemistry [1]. Yet, classical transition state theory is lacking on at least two accounts. First, the fundamental assumption of classical TST is based on the notion that the recrossings of trajectories through the transition state can be neglected. Second, the classical TST formulation neglects quantum mechanical effects such as tunneling and mode quantization. Fortunately, the influence of classical recrossings can be accounted for by analytic approaches [2] or with the reactive flux correlation function methodology [3], while quantum effects can be described by semiclassical [4-9] or quantum mechanical [10,11] TST-like approaches (QTST). One of the latter QTST approaches, path integral QTST [10], has also recently been combined by *ansatz* with a reactive flux-like formulation so that *both* recrossing and quantum effects in activated rate processes can be estimated [12]. A different approach within the path integral QTST is based on an analytic theory [13] for the recrossing corrections (i.e., the "transmission coefficient" problem), but the full numerical implementation of the path integral QTST expression is used to determine the quantum corrections to the classical TST rate.

In the present paper, a different semiclassical TST (SCTST) formulation proposed nearly 20 years ago by Chapman, Garrett, and Miller (CGM) [8] is revisited. As it turns out, it is quite illuminating to re-examine this SCTST formulation in the light of several more recent developments in the field of condensed phase activated dynamics [2,3]. To be specific, it will be shown that the CGM semiclassical theory is continuously accurate and stable at temperatures both above *and* below the so-called "crossover" temperature (i.e., the temperature below which the dynamics becomes dominated by tunneling). Moreover, the accuracy of the CGM formula will be shown to be improved by rotation of the TST dividing surface. Finally, and most importantly, the SCTST formula is shown to form the basis for a semiclassical reactive flux algorithm [3] which allows one to estimate both the quantum and dynamical corrections to the classical TST rate constant on the same

footing.

The present paper is organized as follows: In Sec. 2, the basic CGM formulation of a SCTST expression is reviewed and the attributes of the formula are discussed. The semiclassical reactive flux algorithm based on the SCTST formula will also be described. Next, in Sec. 3 several applications of the method will be presented which are designed to test the theory against known results. Concluding remarks are then given in Sec. 4.

2. Theory

A. Semiclassical TST of Chapman, Garrett, and Miller

The basis for the SCTST formulation of CGM [8] is the semiclassical perspective on Boltzmann statistical mechanics developed by Miller [14]. For example, the diagonal matrix elements of the Boltzmann density matrix (i.e., the particle density) are given by

$$\rho(\mathbf{q}) = \langle \mathbf{q} | exp(-\beta H) | \mathbf{q} \rangle \tag{1}$$

where $\beta = (k_B T)^{-1}$. By splitting the Boltzmann operator into a product of two equal parts, and by inserting a complete set of states between those parts, the particle density can be re-written as [14]

$$\rho(\mathbf{q_0}) = \int d\mathbf{q_1} |\langle \mathbf{q_0} | e^{-\beta H/2} | \mathbf{q_1} \rangle|^2 \quad . \tag{2}$$

Upon introduction of the semiclassical limit for the imaginary time propagator elements $\langle \mathbf{q_0} | e^{-\beta H/2} | \mathbf{q_1} \rangle$, the particle density then takes the form [14]

$$\rho(\mathbf{q_0}) = h^{-N} \int d\mathbf{q_1} \, |\partial \mathbf{q_1} / \partial \mathbf{p_0}|^{-1} \, exp \left\{ -\frac{2}{\hbar} \int_0^{\hbar\beta/2} d\tau H[\mathbf{p}(\tau), \mathbf{q}(\tau)] \right\} \quad , \tag{3}$$

where $|\partial \mathbf{q_1} / \partial \mathbf{p_0}|$ is the Jacobian relating the coordinate at imaginary time $\tau_1 = \hbar\beta/2$ to its momentum at imaginary time $\tau_0 = 0$, $H[\mathbf{p}(\tau), \mathbf{q}(\tau)]$ is the value of the Hamiltonian, and N is the dimensionality of the system. The trajectories which are used to calculate the value of the Hamiltonian in eq. (3) are generated by the differential equations

$$\dot{\mathbf{q}}(\tau) = \frac{\partial H}{\partial \mathbf{p}(\tau)} \quad ; \quad \dot{\mathbf{p}}(\tau) = \frac{\partial H}{\partial \mathbf{q}(\tau)} \tag{4}$$

subject to the initial conditions $\mathbf{q}(0) = \mathbf{q}_0$ and $\mathbf{p}(0) = \mathbf{p}_0$. From eq. (4), it is seen that the trajectories are propagated on the upside-down potential, $-V(\mathbf{q})$, and thereby have excursions into the classically forbidden regions of the potential.

An insightful trick due to Miller [14] is to perform a change of variables from the differential final position elements $d\mathbf{q}_1$ to the differental initial momentum elements $d\mathbf{p}_0$. The Jacobian factor from this transformation cancels the Jacobian factor in eq. (3) and one is left with only an integration over initial momenta. This step in itself is a simplifying feature since the calculation of the semiclassical canonical density no longer requires the solution of a classical trajectory problem having double ended boundary conditions. For example, the semiclassical partition function in Miller's theory is given by [14]

$$\begin{aligned} Q_{SC} &= \int d\mathbf{q}_0 \rho_{SC}(\mathbf{q}_0) \\ &= h^{-N} \int\int d\mathbf{p}_0 d\mathbf{q}_0 exp\left\{ -\frac{2}{\hbar} \int_0^{\hbar\beta/2} d\tau H[\mathbf{p}(\tau), \mathbf{q}(\tau)] \right\} \quad . \end{aligned} \tag{5}$$

Stratt and Miller [15] have noted that the underlying semiclassical phase space distribution function in this theory is given by

$$W_{SC}(\mathbf{p}_0, \mathbf{q}_0) = h^{-N} exp\left\{ -\frac{2}{\hbar} \int_0^{\hbar\beta/2} d\tau H[\mathbf{p}(\tau), \mathbf{q}(\tau)] \right\} \quad . \tag{6}$$

Actually, since Liouville's theory implies the conservation of phase space differential element [i.e., $d\mathbf{q}_0 d\mathbf{p}_0 = d\mathbf{q}(\tau) d\mathbf{p}(\tau)$], then eq. (6) can be rewritten for an arbitrary time shift τ_0 to give the more general semiclassical phase space distribution function [8]

$$W_{SC}(\mathbf{p}_0, \mathbf{q}_0) = h^{-N} exp\left\{ -\frac{2}{\hbar} \int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau H[\mathbf{p}(\tau), \mathbf{q}(\tau)] \right\} \quad . \tag{7}$$

The trajectories used to calculate $H[\mathbf{p}(\tau), \mathbf{q}(\tau)]$ in this distribution function begin with values $(\mathbf{p}_0, \mathbf{q}_0)$ at time $\tau = 0$, then are propagated on the upside-down potential [cf. eq. (4)] backward in time to $\tau = -\tau_0$ and forward in time to $\tau = \hbar\beta - \tau_0$.

The optimal choice of τ_0 in eq. (7) will depend on the quantity which is being averaged. (The semiclassical partition function Q_{SC} in eq. (5), however, is independent of the choice of τ_0 [8].) For example, if one calculates the semiclassical average $\langle q^2 \rangle$ with the distribution in eq. (7) for a simple harmonic oscillator of frequency ω, one finds

$$\langle q^2 \rangle = \frac{\hbar}{2m\omega} \frac{sinh(\hbar\beta\omega - 2\omega\tau_0) + sinh(2\omega\tau_0)}{2sinh^2(\hbar\beta\omega/2)} \quad . \tag{8}$$

For this example, only the choice of $\tau_0 = 0$ or $\hbar\beta/2$ gives the correct answer.

In general, one does not know the optimal choice of τ_0, except for certain analytically solvable models. Based on such information, however, one can *assume* a certain value for τ_0 when using the semiclassical distribution function for non-trivial systems. It is in this same spirit that CGM suggested an approximate SCTST expression for the rate constant [8]. That expression for the forward rate constant of a general system is given by

$$k_{SCTST} = Q_R^{-1} h^{-N} \int \cdots \int d\mathbf{P} d\mathbf{Q} dp dq \, \delta(q^* - q) \frac{p}{m} h(p) \times exp\left\{ -\frac{2}{\hbar} \int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau H[p(\tau), q(\tau), \mathbf{P}(\tau), \mathbf{Q}(\tau)] \right\} \quad , \tag{9}$$

where Q_R is the partition function of the system in the reactant state, q and p are, respectively, the reaction coordinate and its conjugate momentum, $q = q^*$ defines the dividing surface along the reaction coordinate, $h(\cdots)$ is the unit step function, and $\mathbf{Q}$ and $\mathbf{P}$ are all other coordinates and conjugate momenta of the system, respectively. The subscript "0" on the momenta and coordinates in the integrals have been dropped here, but it should be remembered that these variables provide the initial conditions for the trajectories which are propagated forward and backward in time on the upside-down potential in order to calculate $H[p(\tau), q(\tau), \mathbf{P}(\tau), \mathbf{Q}(\tau)]$ in eq. (9).

Based on their analysis of the simple parabolic barrier, CGM concluded that the most reasonable choice of τ_0 in eq. (9) is $\tau_0 = \hbar\beta/4$. More specifically, this choice of τ_0 is the only one that gives the exact rate constant for the parabolic barrier model. Interestingly, this result for the parabolic barrier coincides with the minimum of the flux in eq. (9) with

respect to the choice of τ_0. We therefore suggest, without proof, that the best choice of τ_0 in the SCTST formula [eq. (9)] is the one that minimimizes the imaginary time action in the exponential of eq. (9). For example, at any initial point in the reaction coordinate phase space (p, q), the imaginary time action for a one-dimensional barrier problem is given by

$$S(\tau_0) = \int_{-\tau_0}^{\hbar\beta/2-\tau_0} H(\tau)d\tau \;=\; E + 2\int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau V_b[q(\tau)] \quad , \tag{10}$$

where E is the conserved energy of the particle moving on the inverted barrier potential $-V_b(q)$. If the extremum of the action is taken, one obtains the condition for τ_0:

$$V_b[q(-\tau_0)] \;=\; V_b[q(\hbar\beta/2-\tau_0)] \quad . \tag{11}$$

Thus, the condition of $\tau_0 = \hbar\beta/4$ can be derived from eq. (11) for a symmetric barrier uncoupled to a bath. In view of the additional complications in solving eq. (11) for the most general case, the choice of $\tau_0 = \hbar\beta/4$ would seem to be a reasonable, or at least an expedient, choice for τ_0 for more complicated unsymmetrical, many-dimensional systems.

Before preceeding to the reactive flux formulation based on eq. (9), some consideration should be given to actual evaluation of the SCTST rate constant for a general condensed phase activated rate process. Clearly, the direct numerical evaluation of the phase space integral in eq. (9) is prohibitively time-consuming for a many-dimensional system. Fortunately, the standard techniques of computer simulation in statistical mechanics can be used. For example one can formulate the evaluation of eq. (9) in terms of a Monte Carlo average by using a reference Hamiltonian, $H_{ref}(\tau)$. Equation (9) is then rewritten as

$$k_{SCTST} \;=\; k_{SCTST}^{ref}\left\langle exp\left[-\frac{2}{\hbar}\int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau\Delta H(\tau)\right]\right\rangle_{ref} \quad , \tag{12}$$

where the average $\langle\cdots\rangle_{ref}$ denotes averaging in the semiclassical flux-weighted distribution function for the reference system [cf. eq. (16) below] and $\Delta H(\tau)$ in eq. (12) is given by

$$\Delta H(\tau) \;=\; H[p(\tau), q(\tau), \mathbf{P}(\tau), \mathbf{Q}(\tau)] \;-\; H_{ref}[p_{ref}(\tau), q_{ref}(\tau), \mathbf{P}_{ref}(\tau), \mathbf{Q}_{ref}(\tau)] \quad . \tag{13}$$

The subscripted variables here refer to the reference system Hamiltonian and the trajectories on that inverted potential [cf. eq. (4) written for the reference system], while the unsubscripted variables refer to the actual system. Equation (12) can, of course, be written as a product over a series of intermediate reference states in the form of a thermodynamic charging algorithm. As an alternative to the reference state/charging procedure, one could instead employ umbrella sampling [16] to calculate the flux-weighted distribution function relative to the reactant state.

As demonstrated by Chapman, Garrett, and Miller [8], the SCTST formula in eq. (9) can describe the tunneling effects in gas phase atom-diatom activated rate processes and, as discussed in the next section, there is every reason to expect the same will be true in the condensed phase. Chapman, et al. also mentioned that one could run classical trajectories to estimate the *dynamical recrossing* effects. These trajectories would be initiated from the top of the barrier with initial conditions weighted by the semiclassical distribution function in eq. (7). Although CGM did not carry out such a calculation, we believe this suggestion has considerable merit, particularly in light of the more recent development of the classical reactive flux correlation function formalism [3]. The latter formalism, which readily carries over to the semiclassical case, allows one to *efficiently* calculate the dynamical corrections to the classical TST rate constant.

In order to develop a semiclassical reactive flux correlation function expression, one must first define a dynamical correction factor κ_{SC} to the SCTST rate constant in eq. (9), i.e.,

$$k_{SC} = \kappa_{SC} k_{SCTST} \quad , \tag{14}$$

where k_{SC} is a semiclassical forward rate constant which includes the transition state recrossing effects relative to the SCTST value of the rate constant. These dynamical effects are quantified in the value of the semiclassical dynamical correction factor κ_{SC}, given as a function of time by

$$\kappa_{SC}(t) \;=\; \langle h[q(t) - q^*] \rangle_{j_{sc}^+} \;-\; \langle h[q(t) - q^*] \rangle_{j_{sc}^-} \quad , \tag{15}$$

where the symbol $\langle \cdots \rangle_{j_{sc}^{\pm}}$ denotes *classical* trajectories $[p(t), q(t), \mathbf{P}(t), \mathbf{Q}(t)]$ which have positive ("+") or negative ("−") initial reaction coordinate momenta. The reactive flux trajectories in eq. (15) have initial conditions generated from a semiclassical flux-weighted distribution function $W_j^{SC}(p, q, \mathbf{P}, \mathbf{Q})$, given by

$$W_j^{SC}(p, q, \mathbf{P}, \mathbf{Q}) \;=\; (Q_R h)^{-N} \delta(q^* - q) \frac{|p|}{2m} exp\left\{ -\frac{2}{\hbar} \int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau H(\tau) \right\} \quad . \tag{16}$$

It should be noted that the classical trace of the semiclassical flux-weighted distribution function yields the SCTST rate constant in eq. (9), i.e.,

$$k_{SCTST} \;=\; Tr_{cl}\left[W_j^{SC}(p, q, \mathbf{P}, \mathbf{Q})\right] \quad . \tag{17}$$

The semiclassical reactive flux correlation function in eq. (15) is calculated (i.e., the trajectories are propagated) until it reaches a "plateau" value [3]. After that point, the value of κ_{SC} is essentially constant and can be easily determined. It should also be noted that the dividing surface in eq. (16) can be optimized to minimize the recrossing effects and hence improve the accuracy of the SCTST rate constant in eq. (17). However, the semiclassical flux through different dividing surfaces may not be invariant with respect to the choice of the dividing surface. This inconsistency can be readily eliminated, albeit at some cost in computational effort (see the Appendix).

Equations (14) and (15) represent a unified computational methodology for describing tunneling effects (via k_{SCTST}) and dynamical recrossing effects (via κ_{SC}) in thermally activated rate processes. There is no doubt that much of the CGM formulation, as well the present reactive flux extension of that theory, has a somewhat *ad hoc* character (i.e., it has not been derived from first principles). To formulate the above equations, or equations like them, using a completely systematic semiclassical analysis will require a new and better understanding of the quantum-classical correspondence principle. This rather substantial challenge will be reserved for future research. However, as will be shown in the next section, the above semiclassical methodology also has many appealing characteristics within the context of quantum activated dynamics, not the least of which is its clear computational

power for studying highly nonlinear, complex systems. In fact, it is the latter feature of the method which mitigates to some degree the lack of rigor in its formulation.

3. Applications

3.1. One-dimensional Barrier Crossing Problems

Much about the characteristics of the basic SCTST formula in eq. (9) can be understood by analysis of a simple one-dimensional barrier crossing problem. For example, CGM have already demonstrated that eq. (9), for the choice of $\tau_0 = \hbar\beta/4$, gives the exact result when the barrier potential $V_b(q)$ is approximated to be an upside-down parabola [i.e., $V_b(q) \simeq V_0 - (1/2)m\omega_b^2(q - q^*)^2$]. This result, however, is essentially a "higher" temperature result, being valid only for temperatures such that $\hbar\beta\omega_b < 2\pi$.

For temperatures below the one-dimensional crossover temperature (i.e., for $\hbar\beta\omega_b \geq 2\pi$), the SCTST formula in eq. (9) can be tested numerically. Indeed, CGM have presented results for the Eckart barrier and for the collinear $H + H_2$ reaction which were in good agreement with the known exact results. But why the good agreement? In this regard, it proves to be quite instructive to carry out a more in-depth analysis of the dominant contributions to the phase space integral in eq. (9) for a non-quadratic barrier potential such as a symmetric Eckart barrier [$V_b(q) = V_0 cosh^{-2}(\alpha q/2)$]. For this (or any) one-dimensional system, the integral over the reaction coordinate q in eq. (9) is, of course, fixed at q^* by the delta-function. The integral over the momentum must be performed, however. These values of momenta provide the initial conditions for the trajectories which are propagated on the upside-down barrier potential, $-V_b(q)$, in the calculation of the exponential weighting function in eq. (9). In fig. 1, the flux-weighted distribution function is plotted for a symmetric Eckart barrier of height 2000 cm^{-1} and lengthscale $\alpha = 5.73$ $Å^{-1}$ at 125 K. It is seen that the distribution function is strongly peaked at a certain value of reaction coordinate momentum given by p_{max}. In fig. 2, the imaginary time trajectory [cf. eq. (4)] on the upside-down Eckart barrier potential is plotted for the initial conditions (p_{max}, q^*), where q^* equals zero in this case. From this initial condition, the trajectory is propagated backward in time to the time $-\tau_0 = -\hbar\beta/4$ and forward in time

to $\tau_0 = \hbar\beta/4$. It is seen from fig. 2 that the trajectory exactly reaches the classical turning point (dashed lines) of the inverted barrier potential. Thus, *this trajectory is precisely the WKB trajectory for tunneling through the barrier*. Stated differently, the trajectory shown in fig. 2 is exactly one-half of the well-known semiclassical periodic orbit, or "kink-pair", trajectory from instanton theory [7,9]. (It should be noted that the SCTST expression in eq. (9) requires only one-half of an instanton periodic orbit because of the factor of two in the exponent.)

Actually, it is no accident that the instanton dynamics dominates the value of the SCTST formula in eq. (9) at low temperatures. In general, a steepest descents analysis of the exponential in eq. (9) below the crossover temperature will locate two dominant contributions to that term: the aforementioned instanton trajectory and the "trivial" stationary trajectory solution for the initial conditions $p = 0$, $q = q^*$. However, the latter contribution to the exponential, which is quite large, *cannot* contribute to the flux-weighted distribution function in eq. (16) which underlies the SCTST expression [eq. (9)]. This feature of the theory arises because the term $|p|$ in the flux-weighted distribution insures a weight of *zero* for the $p = 0$, $q = q^*$ contribution to the semiclassical phase space integral. As a result of this feature, the basic SCTST formula in eq. (9) will always have a value very close to the instanton result for temperatures below crossover. Thus, in view of this low temperature analysis and the higher temperature parabolic barrier analysis [8], it can be concluded that the SCTST formula can be faithfully used at *all temperatures*, providing a stable, continuous theory for the rate constant above, below, and through the crossover region. (This very appealing property is also a characteristic the theory has in common with the path integral QTST [10]). In order to highlight the accuracy of the SCTST formula in eq. (9) as a function of temperature, Table I lists results computed with that formula for the symmetric Eckart barrier quantum corrections versus the known exact results [17].

3.2. A Two-Dimensional Test of the Reactive Flux Method

The previous subsection contains a discussion of the ability of the basic SCTST formula in eq. (9) to accurately describe tunneling effects. In this subsection, a test of the

semiclassical reactive flux formulation in eqs. (14)−(16) is presented. In order to do this, the reactive flux was studied for a non-quadratic barrier potential which is bilinearly coupled to a harmonic oscillator. Exact quantum reactive flux results exist for this system [18], and it has also been studied by other approximate methods. The Hamiltonian used in these studies is given by

$$H = \frac{p^2}{2\mu} + \frac{P^2}{2\mu} + V_b(q) + \frac{\mu}{2}\omega^2(Q - cq)^2 \quad , \tag{18}$$

where μ is a reduced mass, c is the coupling between modes, and ω the bath mode frequency. The reaction coordinate potential was chosen to be a symmetric Eckart potential

$$V_b(q) = V_0 sech^2(\alpha q/2) \quad . \tag{19}$$

where α is a length parameter, V_0 is the barrier height, and the frequency of motion on the top of the Eckart barrier is defined by $\omega_b^2 = -\alpha^2 V_0/(2\mu)$.

The coupling constant c in eq. (18) was determined by the first term in a cosine Fourier representation of a Gaussian friction kernel such that [18]

$$\begin{aligned} c^2 =& \frac{1}{\mu\omega^2}\frac{2}{\tau_{bath}}\int_0^{\tau_{bath}} dt cos(\omega t)\eta(t) \\ =& \frac{2f|\omega_b|\sigma^2}{\tau_{bath}}\ \frac{exp[-(\omega\sigma)^2/2]}{(\omega\sigma)^2} \quad . \end{aligned} \tag{20}$$

where σ determines the timescale of the friction kernel. The variable f here is a reduced friction parameter, given by $\eta_0/\mu|\omega_b|$, and η_0 is the zero time value of the friction.

In the calculations, the barrier height was taken to be 3425.3 cm^{-1}, the lengthscale α to be 3.97 $Å^{-1}$, the reduced mass μ equal to 0.672 amu, and the barrier frequency ω_b to be 1164.0 cm^{-1}. For the bath, the decay parameter σ was chosen to be 86.6 fs and the bath fequency ω to be 48 cm^{-1}. The timescale parameter τ_{bath} in eq. (20) was set equal to 2σ. (This model is referred to as the "slow friction" in ref. [18].) In the calculations, 2000 sets of initial conditions were generated using the SC flux weighted distribution function in eq. (16). From this set of initial conditions, 2000 trajectories were then run, each for 1 ps, to

calculate κ_{SC} from eq. (15). The calculations were performed at temperatures of 200K and 300K.

As can be seen from Figs. 3 and 4, the combined semiclassical theory in eqs. (14)−(16) (i.e., SCTST with reactive flux corrections) is in very good agreement with the exact quantum results. On the other hand, the SCTST rate constant alone is not in good agreement with the exact results. One can conclude, therefore, that the inclusion of the semiclassical dynamical correction factor in eq. (15) is essential for the accuracy of the method at large couplings. At intermediate couplings, the semiclassical reactive flux result drops drops too far below the exact results, particularly at 200 K. This regime is due to an interesting, but pathological, feature of this two-mode problem which leads to metastable trapped classical trajectories in the transition state region. Such trapping regions in phase space are far more pronounced in two-dimensional potentials for which locally integrable classical motion can rigorously segment phase space into disjoint regions [19]. In many-dimensional condensed phase systems, this behavior will be far less likely to occur.

3.3. Parabolic Barrier Coupled to a Multidimensional Bath Model

To this point in the present manuscript, the SCTST rate constant and SC reactive flux method have been applied to low-dimensional test cases. These models were chosen, of course, because exact results are essentially non-existent for many-body quantum activated rate problems. One exception to this rule, however, is the many-dimensional parabolic barrier potential. This potential is given by

$$V(q,\mathbf{Q}) \;=\; V_0 - \frac{1}{2}m\omega_b^2 q^2 + \sum_{i=1}^{N_{osc}} \frac{1}{2}m_i\omega_i^2 \left(Q_i + \frac{c_i}{m_i\omega_i^2}\,q\right)^2 \quad , \tag{21}$$

where ω_b is the magnitude of the unstable barrier frequency, the constants c_i are the coupling constants between the reaction coordinate and the bath modes, and the bath mode frequencies and masses are given by ω_i and m_i, respectively. The bath modes in the above Hamiltonian are chosen to model the linear force fluctuations from a bath on the reaction coordinate [20].

For relatively few degrees of freedon, the multidimensional parabolic barrier problem

is trivial because a normal coordinate rotation can be readily performed to separate the true unstable reactive normal mode ρ from the stable orthogonal vibrations $\{y_j\}$. However, for an *infinite* number of bath oscillators as in condensed phase problems, the normal mode transformation can only be defined formally. Even so, if such a transformation is performed to find the many-dimensional set of normal modes, then the SCTST in eq. (9) can still be applied to the Hamiltonian arising from eq. (21), but with the dividing surface chosen to be along the true multidimensional reactive mode ρ [21,22] rather than along the "simple" reaction coordinate q as is written in eq. (9). In this case, the result for the rate constant can be obtained analytically and is given by the exact result [22]:

$$k_{SCTST} = \frac{k_B T}{hQ_R} \frac{\hbar\beta\lambda_0^\ddagger/2}{sin(\hbar\beta\lambda_0^\ddagger/2)} \prod_{j=1}^{N_{osc}} \frac{1}{2sinh(\hbar\beta\lambda_j/2)} exp(-\beta V_0) \quad , \tag{22}$$

where $\lambda_0^\ddagger$ is the magnitude of the frequency of the multidimensional reactive normal mode and the frequencies $\{\lambda_j\}$ are the frequencies of the stable modes orthogonal to the reaction coordinate. The continuum ($N_{osc} \rightarrow \infty$) limit of the multidimensional parabolic result is given by [22,23]

$$k_{SCTST} = \frac{k_B T}{hQ_R} \frac{\lambda_0^\ddagger}{\omega_b} \prod_{n=1}^{\infty} \frac{1}{\Omega_n^2 - \omega_b^2 + \Omega_n \hat{\eta}(\Omega_n)/m} exp(-\beta V_0) \quad , \tag{23}$$

where Ω_n equals $2\pi n/\hbar\beta$, $\hat{\eta}(\cdots)$ is the Laplace transform of the friction kernel along the coordinate q, and $\lambda_0^\ddagger$ is given from the solution of the well-known Grote-Hynes relationship [24]

$$\lambda_0^\ddagger = \frac{\omega_b^2}{\lambda_0^\ddagger + \hat{\eta}(\lambda_0^\ddagger)/m} \quad . \tag{24}$$

The result in eq. (23) can be shown [23] to provide an accurate description of quantum activated dynamics for reactive systems coupled to linearly responding condensed phase environments which are above the multidimensional crossover temperature (i.e., for $\hbar\beta\lambda_0^\ddagger < 2\pi$).

The result in eq. (23) is, of course, the exact result [22,23]. It is therefore concluded that a rotation of the dividing surface in the basic SCTST rate constant expression can

improve the accuracy of the theory—at least for the parabolic system. The question arises, however, as to whether a calculation using the semiclassical reactive flux method with a flux-weighted distribution function for an *unrotated* dividing surface [cf. eq. (16)] will achieve the same result. As it turns out, such a calculation will always give the exact rate constant. To prove this, one first transforms the multidimensional quadratic Hamiltonian for the potential in eq. (21) into the separable normal mode form [21,22]

$$H = \frac{1}{2}(p_\rho^2 - \lambda_0^{\ddagger 2}\rho^2) + \frac{1}{2}\sum_{j=1}^{N_{osc}}(p_j^2 + \lambda_j^2 y_j^2) \quad , \tag{25}$$

where, for convenience, V_0 in eq. (21) is taken to be zero. Since the Hamiltonian is separable in this coordinate system, one can readily uncover the initial conditions for the trajectories which will always proceed from reactants to products. These conditions are represented by the characteristic function $\chi(p_\rho, \rho) = h(p_\rho)h(p_\rho^2 - \lambda_0^{\ddagger 2}\rho^2)$, where $h(\cdots)$ is the unit step function. This function simply states that any trajectory with an initial positive momentum along the true multidimensional reaction coordinate ρ and an energy above the barrier along that coordinate will be reactive (i.e., it will contribute a weight of unity). The calculation of the semiclassical reaction rate from eqs. (14) – (17) is then equivalent to averaging the characteristic function with the semiclassical flux-weighted distribution function in eq. (16). A somewhat lengthy, but straightforward, evaluation of Gaussian integrals then leads to the result that the semiclassical reactive flux calculated with the semiclassical procedure specified by eqs. (14) – (17) will be *exact* for the many-dimensional parabolic model.

Results are shown in Fig. 5 for the numerically determined (exact) transmission coefficient for the parabolic barrier model with a barrier frequency of 1000 cm^{-1} and a 100 discrete oscillator bath [25]. The bath was chosen to model an exponential friction kernel with a decay constant of $4\omega_b^{-1}$. The strength of the friction is characterized here by the dimensionless quantity $\eta(0)/m\omega_b^2$, where $\eta(0)$ is the zero time value of the friction kernel. The reactant partition function was assumed to be given by a harmonic oscillator potential along the q direction with a frequency of $\sqrt{2}\omega_b$ which is also coupled to the oscillator bath. The numerical stability and relative simplicity of this multidimensional calculation bodes

well for applications of the semiclassical method to other, more complicated, many-body systems—at least above the crossover temperature.

3.4. Escape from a Metastable Well in a Dissipative Medium

Rips and Pollak [26] have presented a theory for the quantum mechanical escape rate of a particle out a metastable well in the presence of a dissipative medium. Their theory is valid in the case of a linearly responding bath and for temperatures above the multidimensional crossover temperature. The Rips-Pollak expression for the quantum mechanical escape rate is given by [26]

$$k = \frac{\omega_0}{2\pi}\frac{\lambda_0^{\ddagger}}{\omega_b}\,\Xi\,\Upsilon\,exp(-\beta V_0) \quad , \tag{26}$$

where V_0 is the barrier height, ω_0 is the well frequency, ω_b is the barrier frequency, and $\lambda_0^{\ddagger}$ is the Grote-Hynes reactive frequency [cf. eq. (24)]. The factor Ξ in eq. (26) accounts for the particle tunneling in the presence of the dissipation and, following the notation in eq. (23), is given by

$$\Xi \;=\; \prod_{n=1}^{\infty} \frac{\Omega_n^2 + \omega_0^2 + \Omega_n\hat{\eta}(\Omega_n)/m}{\Omega_n^2 - \omega_b^2 + \Omega_n\hat{\eta}(\Omega_n)/m} \quad . \tag{27}$$

The important new feature in the Rips-Pollak expression is the quantum mechanical depopulation factor Υ, given by

$$\Upsilon \;=\; exp\left[\frac{\beta\hbar\lambda_0^{\ddagger} sin(\beta\hbar\lambda_0^{\ddagger}/2)}{2\pi}\int_{-\infty}^{\infty} d\tau\; \frac{ln[1-\tilde{P}(\tau - i/2)]}{cosh(\tau\beta\hbar\lambda_0^{\ddagger}) - cos(\beta\hbar\lambda_0^{\ddagger}/2)}\right] \quad . \tag{28}$$

In this equation, $\tilde{P}(\tau - i/2)$ is the Fourier transform of the quantum mechanical transition probability, given in terms of the set of stable normal mode frequencies $\{\lambda_j\}$ by

$$\tilde{P}(\tau - i/2) \;=\; exp\left[-\sum_{i=1}^{N_{osc}} \frac{\nu_i[cosh(\beta\hbar\lambda_i/2) - cos(\tau\beta\hbar\lambda_i)]}{sinh(\beta\hbar\lambda_i/2)}\right] \quad , \tag{29}$$

where the quantities ν_i are given by

$$\nu_i = \frac{g_i^2}{2\hbar\lambda_i}\left|\int_{-\infty}^{+\infty} dt_1 e^{i\lambda_i t_1} F(t_1)\right|^2 \quad . \tag{30}$$

The term $F(t)$ here is the time-dependent zero-order force acting on the unstable normal mode ρ such that

$$F(t) = -u_{00} m^{-1/2} \left.\frac{\partial V_{NL}(q)}{\partial q}\right|_{q=m^{-1/2}u_{00}\rho} \quad , \tag{31}$$

where $V_{NL}(q)$ is the nonlinear part of the barrier potential, defined as $V_{NL} = V_b(q) + (1/2)m\omega_b^2 q^2$. The projection of the barrier coordinate q onto the unstable multidimensional normal mode ρ and the stable normal modes $\{y_i\}$ is determined by the transformation [21]

$$\sqrt{m}q = u_{00}\rho + \sum_{i=1}^{N_{osc}} u_{i0} y_i \quad . \tag{32}$$

The constants g_i in eq. (30) are defined by the relation $g_i \equiv u_{i0}/u_{00}$. More details about the Rips-Pollak theory can be found in ref. [26].

The present semiclassical reactive flux formalism was applied to a cubic barrier potential coupled to a linearly responding bath with an exponential friction kernel. The potential along q was given by

$$V_b(q) = V_0 - \frac{1}{2}m\omega_b^2 q^2 - \frac{a}{3}q^3 \quad , \tag{33}$$

where $a^2 = (m\omega_b^2)^3/6V_0$. In the simulations, the barrier height V_0 was given a value of 3425.3 cm^{-1} and the relevant particle frequencies were chosen to be $\omega_b = \omega_0 = 1000\ \text{cm}^{-1}$. The linearly responding bath was modeled by 100 harmonic oscillators as in our earlier work on classical activated dynamics [25]. The exponential decay timescale of the bath friction kernel was chosen to be 4 ω_b^{-1}. As in Sec. 3.3, the strength of the friction was characterized by the dimensionless quantity $\eta(0)/m\omega_b^2$, where $\eta(0)$ is the zero time value of the friction kernel.

The results from the semiclassical reactive flux calculations for the cubic well model are depicted in Fig. 6 and compared to the analytic results from the Rips-Pollak theory. Also

shown for comparison are the analytic classical result from the theory of Pollak, Grabert, and Hänggi (PGH) [27]. As in the classical theory, there are two mechanistic pictures required to analyze the escape rate of the particle from the well as a function of friction strength [2]. At low friction, the dynamics is determined by the rate of energy exchange between the particle in the well and the bath. As the coupling increases in this regime, the rate increases. At high frictions, thermal equilibrium is maintained in the well and the rate is determined by passage over (or through) the barrier. Therefore, at high frictions, the rate decreases as the coupling increases. This phenomenology is, of course, the standard Kramers picture of activated dynamics [28], and the quantum mechanical modifications of that behavior are evident from Fig. 6. The agreement between the SC reactive flux and Rips-Pollak theory is quite encouraging and again suggests that the semiclassical theory will be useful for complicated condensed phase problems.

3.5. Double Well in a Linearly Responding Dissipative Bath

As a final test of the SCTST and the semiclassical reactive flux formalism, the rate constant was calculated in the region of the crossover temperature for a double well barrier potential coupled to a linearly responding bath. The crossover temperature in this case can be estimated by the usual relationship

$$T_{cr} = \hbar\lambda_0^{\ddagger}/(2\pi k_B) \quad , \tag{34}$$

where $\lambda_0^{\ddagger}$ is the Grote-Hynes reactive frequency in eq. (24). In these calculations, a quartic double well was employed of the form

$$V_b(q) = V_0 - \frac{1}{2}m\omega_b^2 q^2 + \frac{m^2\omega_b^4}{16V_0}\, q^4 \quad . \tag{35}$$

This quartic double well has the property that the well frequency, ω_0, is related to the barrier frequency, ω_b, such that $\omega_0 = \sqrt{2}\,\omega_b$.

The specific values of the paramters were again $\omega_b = 1000$ cm^{-1} and $V_0 = 3425.35$ cm^{-1}. The bath was again modeled by 100 discrete oscillators [25], having a friction kernel with timescale $4\omega_b^{-1}$ and strength $\eta_0/\mu\omega_b^2 = 1.0$. For this value of the friction, the unsta-

ble normal mode frequency $\lambda_0^{\ddagger}$ is $\sim$ 530 cm^{-1}; the corresponding crossover temperature being $\sim$ 125 K. Semiclassical calculations were then performed at 100K, 125K, and 150K. The results for the semiclassical rate constant [eq. (14)] and the semiclassical transmission coefficient [eq. (15)] are tabulated in Table II. For the sake of comparison, the semiclassical transmission coefficient at 300 K was found to have a value of 0.68. There are no exact quantum results here with which to compare the semiclassical calculations, but the semiclassical transmission coefficient exhibits an interesting drop in value as the temperature is lowered through the crossover temperature. This result is in general agreement with the behavior predicted by an analytic theory [13] for the transmission coefficient in path integral QTST below the crossover temperature.

4. Concluding Remarks

In the present paper, a semiclassical transition state theory proposed by Chapman, Garrett, and Miller [8] has been "rediscovered" and analyzed within the context of condensed phase reaction rate theory. For the cases studied, it was found that the basic SCTST formula [eq. (9)] is capable of accurately treating activated rate processes over a wide range of temperatures, including in the strongly tunneling regime. The relationship of the theory to the more widely known instanton theory [7,9] has also been elaborated. A significant extension of the theory to include dynamical dividing surface recrossing effects has been presented in the form of a semiclassical reactive flux correlation function formalism [eqs. (14)−(16)]. The accuracy of this formalism was tested against several model and analytical results and found to be quite good. The great strength of the method is the ease with which it can be numerically applied to nonlinear, many-body systems. Moreover, many of the molecular dynamics and Monte Carlo sampling techniques from statistical mechanics can be combined with the formalism. The method is likely to be broadly applicable to a variety of important problems, including proton transfer, adiabatic electron transfer, and the diffusion hydrogen on material surfaces. Some of these applications will be reported in future publications.

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Appendix

As stated in the main text, one can imagine an optimization of the dividing surface in eq. (16) to minimize recrossing effects in the calculation of the semiclassical transmission coefficient [eq. (15)]. In such a procedure, however, the semiclassical flux may not be invariant with respect to the choice of the dividing surface—as it must be in an exact calculation. Although this negative aspect of the formulation will probably not introduce major errors, one can in fact modify the method to make the flux independent of the dividing surface. In order to do this, a semiclassical effective Hamiltonian can be defined as

$$H_{eff}^{SC} = -k_B T \, ln \, [W_{SC}(\mathbf{p}, \mathbf{q})] \quad , \tag{A1}$$

where the semiclassical density $W_{SC}(\mathbf{p}, \mathbf{q})$ is given by eq. (7). This effective Hamiltonian is then used to generate the recrossing trajectories in the calculation of the semiclassical transmission coefficient [eq. (15)]. The equations of motion are given in this case by Hamilton's equations, but with the classical Hamiltonian replaced by the semiclassical effective Hamiltonian H_{eff}^{SC}. Clearly, solving these equations will be more computationally demanding than the usual classical equations.

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TABLE I. Comparison of Tunneling Corrections for the Symmetric Eckart Barrier.

Temperature	SCTST Results[a]	Exact Results[b]
125.6	1686.0	1970.0
150.7	144.4	162.0
188.3	20.3	22.0
251.1	4.9	4.2
301.3	2.9	3.1
376.7	2.0	2.1
502.2	1.5	1.5
753.3	1.2	1.2

[a]Equation (9)

[b]From ref. [17].

TABLE II. Rate Results for the Double Well in a Dissipative Bath.

Temperature	κ_{SC}[a]	Rate (s^{-1})[b]
150	0.91	1.5×10^{-2}
125	0.87	7.9×10^{-4}
100	0.40	2.0×10^{-8}

[a]Equation (15). The numerical error is 5% on the two higher temperature results and 20% on the lowest.

[b]Equation (14)

Figure Captions

Fig. 1: A plot of the semiclassical flux-weighted distribution function [eq. (16)] as a function of initial momentum for a symmetric Eckart barrier at $T = 125K$.

Fig. 2: The imaginary time trajectory on the upside down Eckart potential corresponding to the initial condition $(p_{max}, 0)$ which give the maximum value of the flux-weighted distribution function in Fig. 1. The trajectory is propagated forward in time to $\hbar\beta/4$ and backward in time to $-\hbar\beta/4$. The dashed lines are the classical turning points on the inverted Eckart barrier potential for this initial condition.

Fig. 3: Plots of the reactive flux for the two-dimensional model in Sec. 3.2. The results are from the SCTST expression [eq. (9)], the semiclassical expression which includes the semiclassical transmission coefficient [eq. (14)], and exact quantum wavepacket calculations [18] at 200K.

Fig. 4: Same as in Fig. 3, but for a temperature of 300K.

Fig. 5: A plot of the numerically determined semiclassical rate constant [eq. (14)] for a parabolic barrier potential linearly coupled to 100 bath oscillators as a function of the friction. The solid line is the exact analytic result. The reactant partition function is assumed here to be for a harmonic oscillator potential coupled to the same bath as at the barrier.

Fig. 6: A comparison of the rate constant for a metastable cubic well in a dissipative 100 oscillator bath as calculated from the Rips-Pollak, PGH, and semiclassical [eq. (14)] theories at 300K (see Sec. 3.4).

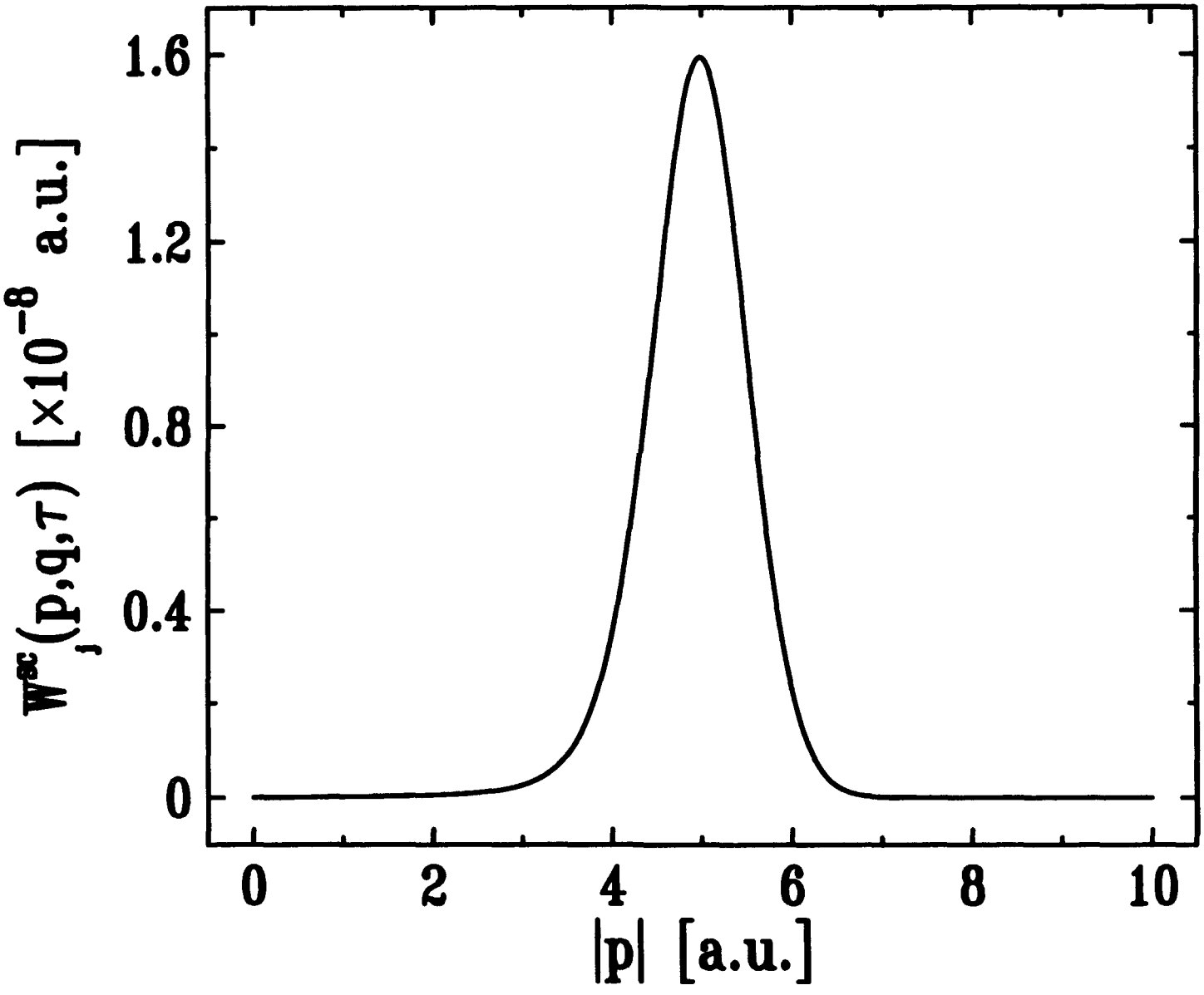

FIGURE 1

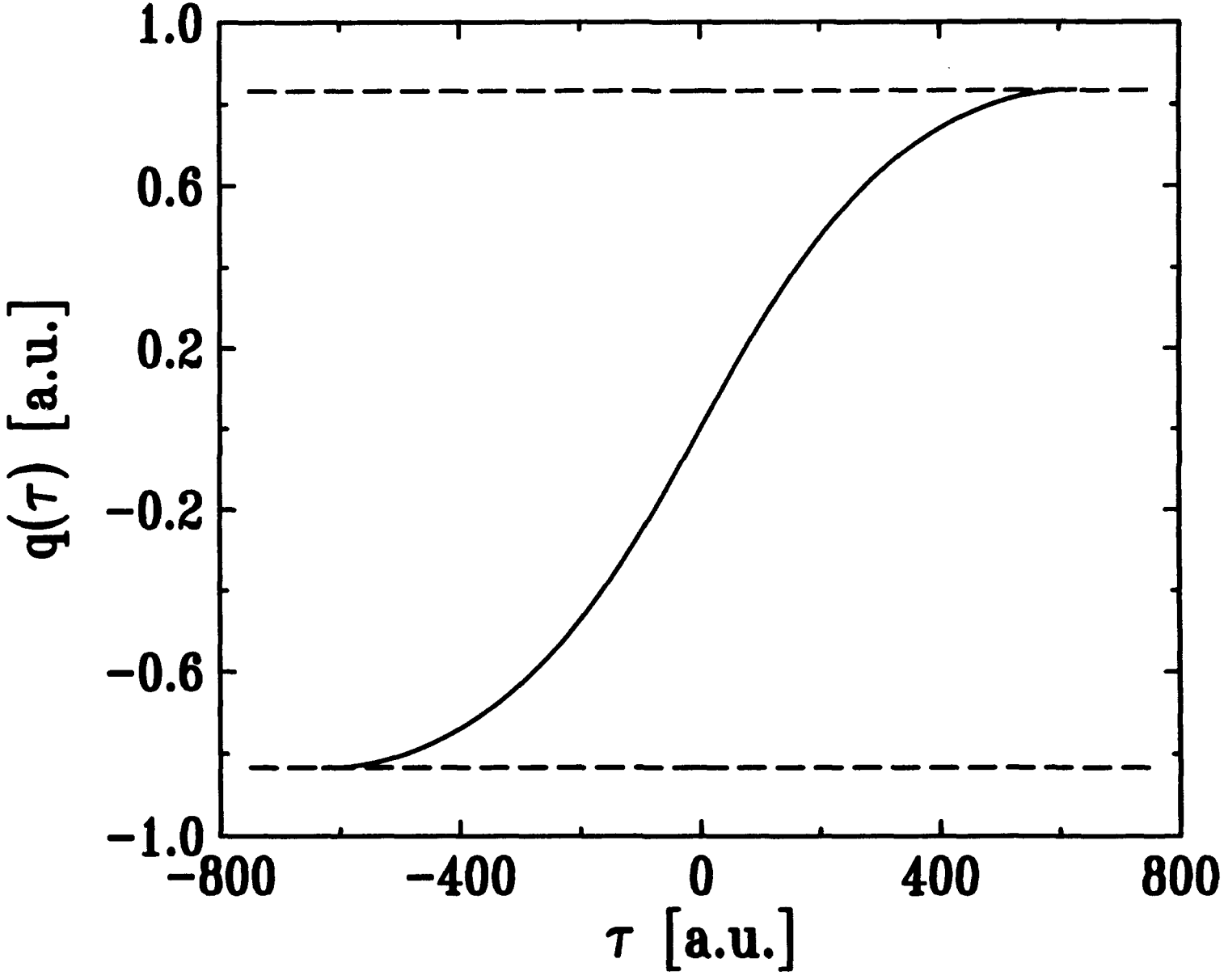

FIGURE 2

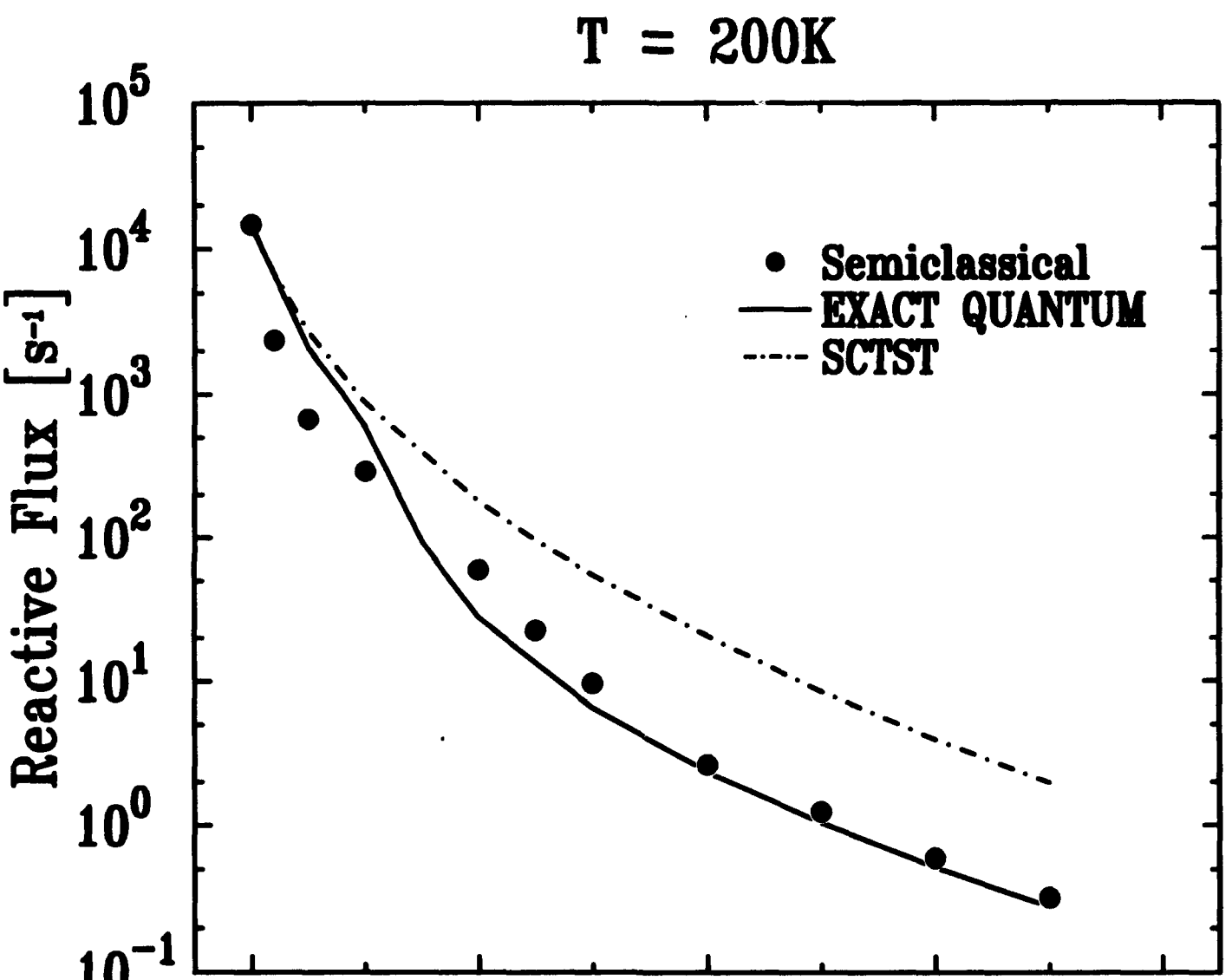
T = 200K
Reactive Flux [s⁻¹]
10⁵
10⁴
10³
10²
10¹
10⁰
10⁻¹
0
20
40
60
80
η(0)/(μ|ω_b|)
Semiclassical
EXACT QUANTUM
SCTST

FIGURE 3

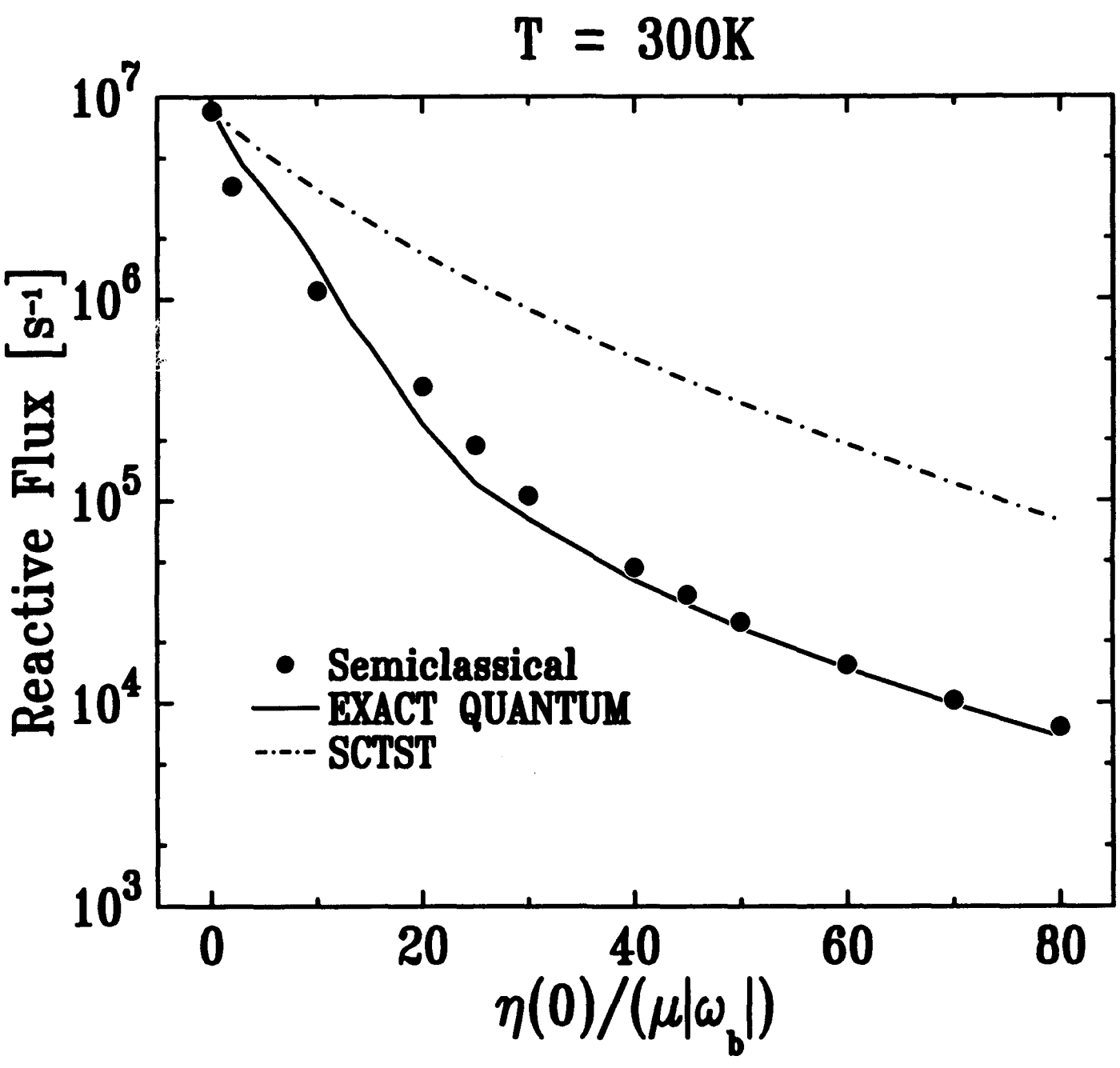
T = 300K
Reactive Flux [s⁻¹]
10⁷
10⁶
10⁵
10⁴
10³
0
20
40
60
80
η(0)/(μ|ω_b|)
Semiclassical
EXACT QUANTUM
SCTST

FIGURE 4

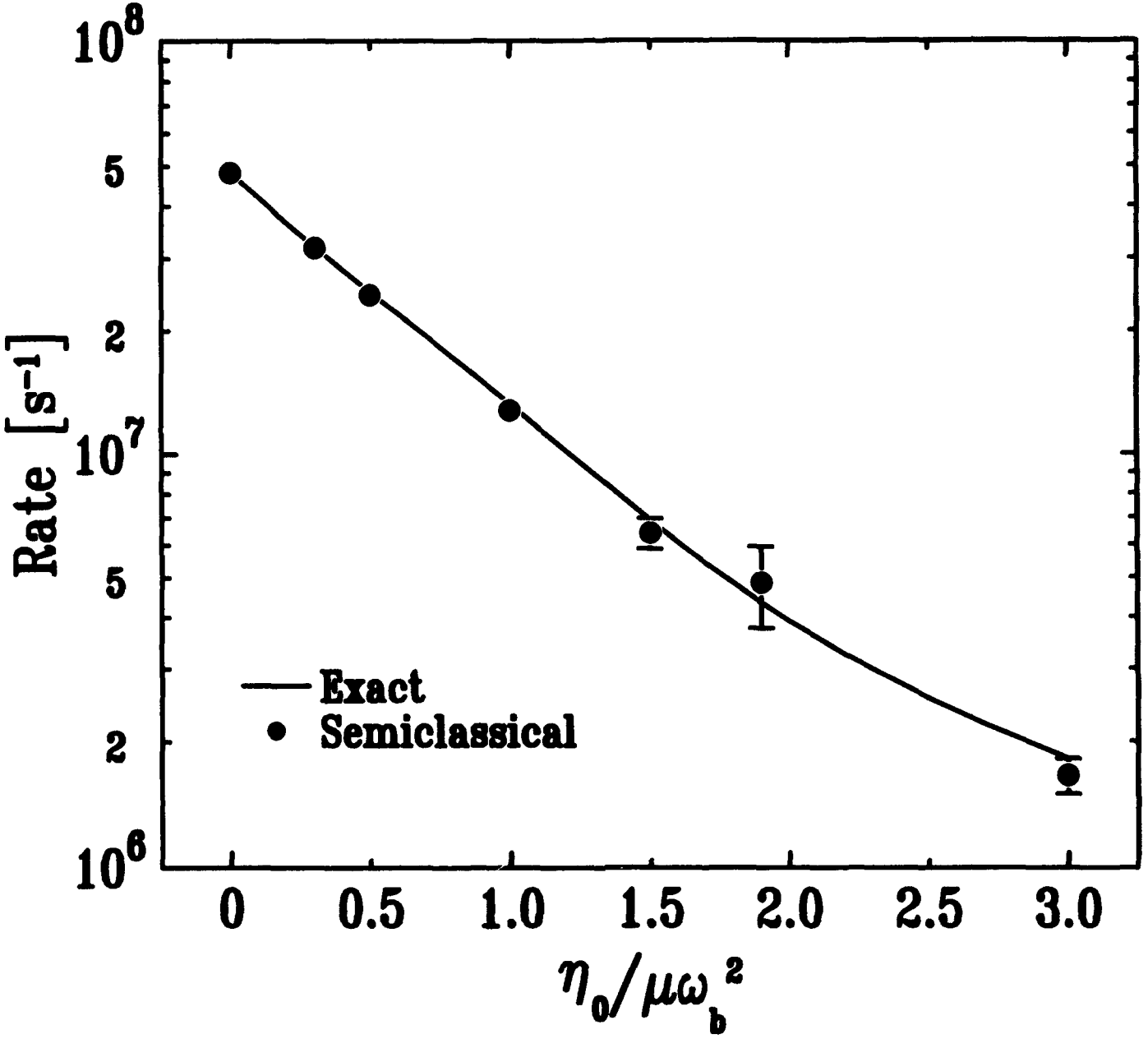
10^8
5
2
10^7
5
2
10^6
Rate [s^{-1}]
Exact
Semiclassical
0
0.5
1.0
1.5
2.0
2.5
3.0
$\eta_0/\mu\omega_b^2$

FIGURE 5

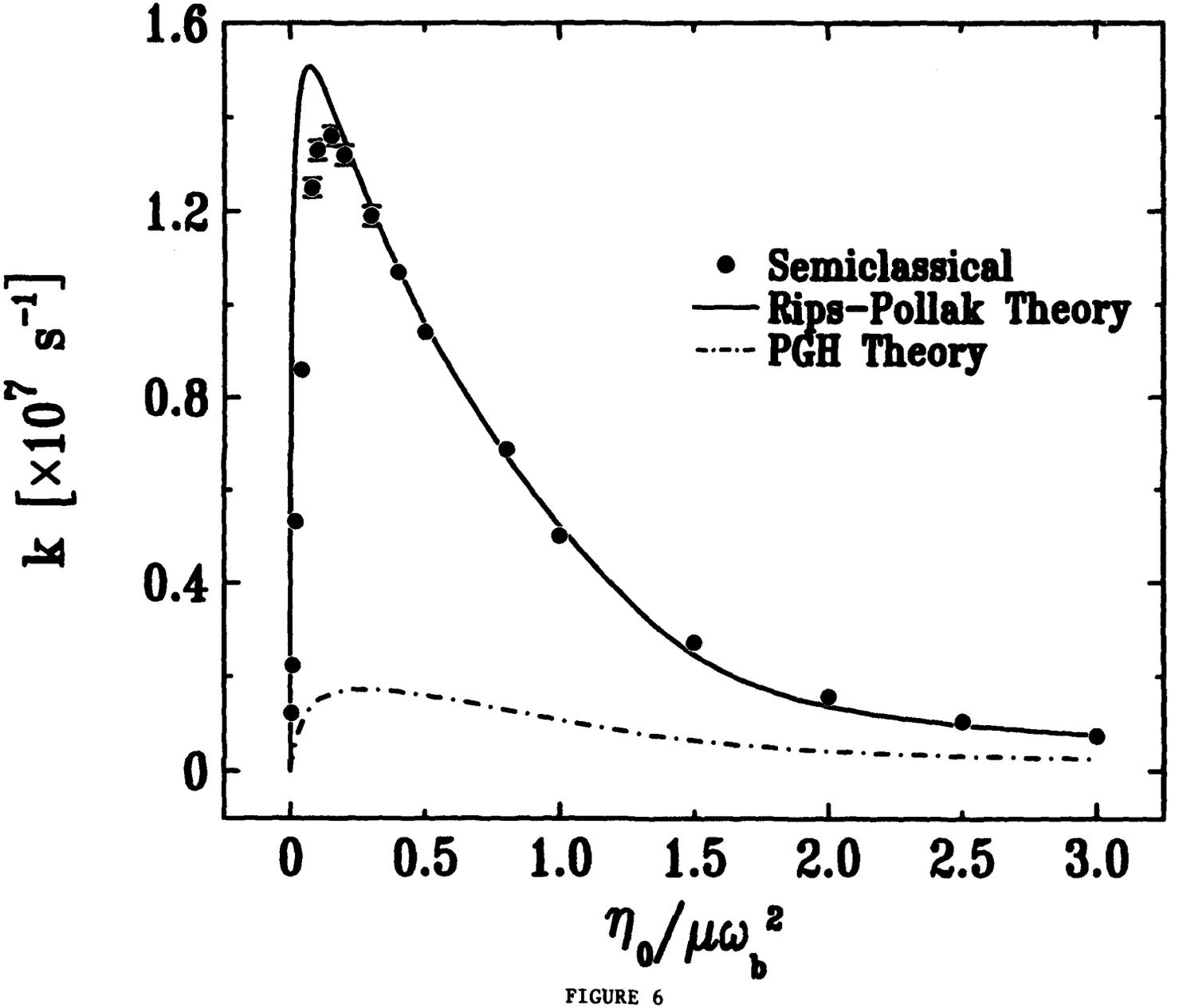
1.6
1.2
0.8
0.4
0
k [×10^7 s^-1]
0
0.5
1.0
1.5
2.0
2.5
3.0
η0/μωb^2
Semiclassical
Rips-Pollak Theory
PGH Theory

FIGURE 6